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Electron Delocalization from the Fullerene Attachment to the Diiron Core within the Active-Site Mimics of [FeFe]Hydrogenase

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Supporting Information

ABSTRACT: Attachment of the redox-active $C_{60}(H)PPh_2$ group modulates the electronic structure of the Fe_2 core in $[(\mu\text{-bdt})Fe_2(CO)_5(C_{60}(H)PPh_2)]$. The neutral complex is characterized by X-ray crystallography, IR, NMR spectroscopy, and cyclic voltammetry. When it is reduced by one electron, the spectroscopic and density functional theory results indicate that the Fe_2 core is partially spin-populated. In the doubly reduced species, extensive electron communication occurs between the reduced fullerene unit and the Fe_2 centers as displayed in the spin-density plot. The results suggest that the [4Fe4S] cluster within the H cluster provides an essential role in terms of the electronic factor.

Proton reduction/hydrogen oxidation is an important process for energy cycling in biological systems. For a variety of metalloenzymes, a subsidiary unit named hydrogenase facilitates enzymatic reactions via the mediation of hydrogen and reducing power. Understanding how hydrogenases utilize protons, electrons, and molecular hydrogen in an effective manner will assist chemists in the task of easing the emerging energy crisis. Among the classes of hydrogenases, [FeFe]hydrogenase is the most intriguing target according to its high turnover frequency of hydrogen production (9000 molecules/s) at mild working potentials (−0.1 to −0.5 V vs SHE).[1] Numerous Fe_2S_2 complexes have been prepared in recent years to model the active site of [FeFe]hydrogenase.[2] As indicated by synthetic work,[3] computational simulations,[4] and biophysical studies,[5] the aza nitrogen cofactor and rotated geometry of the distal Fe center are mainly responsible for the high catalytic efficiency.

Less studied is the role of FeS clusters attached to the Fe_2S_2 core within a H cluster.[6] It is proposed that the [4Fe4S] attachment serves as a hub for electrons shuttling between the Fe_2S_2 catalytic center and the interior FeS clusters 12−14 Å away.[7] Similar to the mitochondrial electron-transport cascade, electron flux flows between the H and F clusters from one site to the other in lower energy. The question is, how is electron transfer between the [4Fe4S] attachment and the Fe_2 site initiated? Recent results indicate that proton reduction requires a relatively negative working potential in diiron carbonyl complexes and even more negative in the phosphine-substituted derivatives. To accommodate the potential difference between the sole $\{(\mu\text{-adt})Fe_2(CO)_3(CN)_2\}$ unit (adt = azadithiolate) and the H cluster if voltammetric results of the synthetic models are taken for reference, ligation of the [4Fe4S] unit to the Fe_2 core serves the purpose more than merely the structural one (Figure 1).[8]

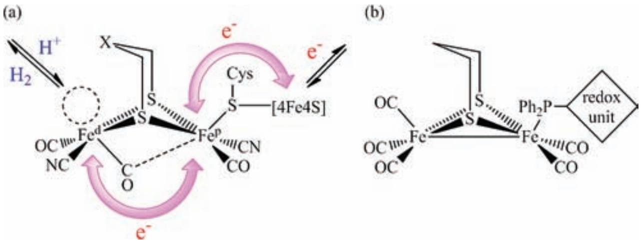

Figure 1. (a) Proton−electron-transfer pathway within the active site of [FeFe]hydrogenase and (b) the model complex bearing a redox unit.

C_{60} is a C-based cluster that is able to uptake up to six electrons in solution.[9] In a 1,1,2,2-tetrachloroethane solution, it can undergo one-electron reversible oxidation.[10] In the aspect of redox chemistry, C_{60} acts as an electron reservoir, which mimics the [4Fe4S] unit in the active site of [FeFe]-hydrogenase. Coordination of the fullerene to the Fe_2 core allows one to study the electronic influence exerted by the reduced C_{60} unit. Herein, we report the generation of $[(\mu\text{-bdt})Fe_2(CO)_5(C_{60}(H)PPh_2)]$ (**1**; bdt = 1,2-benzenedithiolate), which is characterized by spectroscopy and X-ray crystallography. Under reducing conditions, the singly reduced species $[(\mu\text{-bdt})Fe_2(CO)_5(C_{60}(H)PPh_2)]^{\bullet -}$ ($[\mathbf{1}]^{\bullet -}$) is spectroscopically characterized at low temperature. The density functional theory calculations indicate that extensive electronic delocalization occurs between the Fe_2 core and the reduced fullerene fragment upon the addition of two electrons. It is suggested that the electronic structure of the Fe_2 center within **1** is modulated by the redox-active fullerene.

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The treatment of $C_{60}(H)PPh_2$ with 1 equiv of $[(\mu\text{-bdt})Fe_2(CO)_6]$ in the presence of Me_3NO results in the formation of complex **1**. The ν_{CO} IR signals of complex **1** have the same band pattern in similar energy with the other phosphine analogues,[11] suggesting a similar structural skeleton for complex **1**. Crystallographic analysis of complex **1** confirms that one of the CO groups is substituted by $C_{60}(H)PPh_2$ (Figure 2). The Fe–Fe bond distance of 2.4894(6) Å is comparable to those of 2.480(2), 2.4767(4), and 2.4917(4) Å in $[(\mu\text{-bdt})Fe_2(CO)_6]$,[12] $[(\mu\text{-bdt})Fe_2(CO)_5(PTA)]$ (PTA = 1,3,5-triaza-7-phosphaadamantane),[13] and $[(\mu\text{-bdt})Fe_2(CO)_5(PPh_3)]$ (Figure S1 in the Supporting Information, SI), respectively. In $[(\mu\text{-bdt})Fe_2(CO)_5(L)]$ (L = $C_{60}(H)PPh_2$, **1**; PPh_3, **2**; PTA) in which the phosphine ligands are of different steric hindrance, coordination of the phosphines at the apical position is mainly governed by the electronic factor. The bulky fullerene fragment does exert some steric influence on the structure. Compared with the dihedral angles between the basal carbonyls (∠C2–Fe1–Fe2–C4 = ∠C3–Fe1–Fe2–C5 = 2.9°), a large distortion between two apical ligands (∠C1–Fe1–Fe2–P1 = 19.8°) is observed.

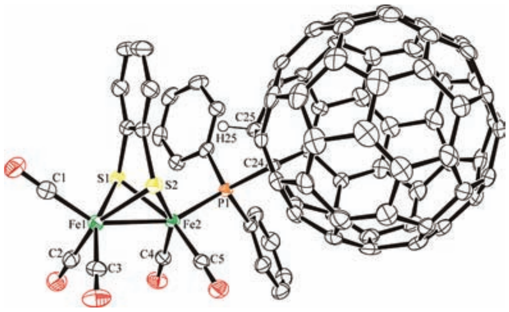

Figure 2. Molecular structure of **1**. Only the hydrogen atom on fullerene is shown for clarity. Selected bond length (Å) and angles (deg): Fe–Fe, 2.4894(6); Fe–S, 2.2749(8); Fe–$C_{CO,ap}$, 1.800(3); Fe–$C_{CO,ba}$, 1.790(3); Fe–P, 2.2449(8); C24–C25, 1.588(4); S–Fe–S, 80.24(3); S–Fe–Fe, 56.83(2); Fe–S–Fe, 66.34(2).

Four reversible reduction events are recorded for **1** under N_2 at 256 K in the accessible electrochemical window of the CH_2Cl_2/*o*-dichlorobenzene (*o*-DCB) solution (Figure 3a). The first, second, and fourth one-electron processes at −1.11, −1.48, and −2.14 V (vs Fc/Fc^+), respectively, are ascribed to the C_{60}-based reductions by comparison with redox pairs of C_{60} and $H_3BC_{60}(H)PPh_2$.[14] The third reduction at −1.78 V is assigned to the Fe-centered redox process. Its larger ΔE value (the difference of E_{pc} and E_{pa}) of 0.24 V, compared to 0.14 and 0.12 V for the other three redox events and the internal Fc/Fc^+ reference pair, respectively, suggests the occurrence of potential inversion.[15] The Fe^IFe^I unit is initially singly reduced, which triggers structural rearrangement with the most possible scenario: rupture of the Fe–S bond.[16] A new thermodynamically stable species is achieved, which is reduced at the potential close to the precedent reduction. Similarly, potential inversion appears to occur upon removal of one electron from the Fe^IFe^I subset at E_{pa} = +0.69 V. Oxidation of the C_{60} unit occurs at +1.35 V. Like its parent fullerene molecule in the solution other than 1,1,2,2-tetrachloroethane, it is an irreversible redox process.[17]

Because of thermal instability, the red-brown product resulting from the treatment of **1** with 1 equiv of Cp_2Co, presumably $[\mathbf{1}]^{\bullet-}$, was characterized solely by spectroscopic methods. The pattern of the FTIR signals remains unchanged, indicating no structural modification at low temperatures in the singly reduced state. A shift of the ν_{CO} bands by 5 cm^{-1} to lower energy (2047 vs, 1990 vs, 1978 s, 1938 w cm^{-1}) confirms that the added electron is mainly localized at the fullerene unit at low temperature (Figure S4 in the SI). Reduction of **1** by sodium in the presence of dibenzo-18-crown-6 ether at −70 °C slowly led to a thermally sensitive green complex $[(\mu\text{-bdt})Fe_2(CO)_5(C_{60}PPh_2)]^-$ ($[\mathbf{3}]^-$). Preparation of $[\mathbf{3}]^-$ is also achieved by the reaction of **1** and 1 equiv of KO^tBu at low temperature (Figure 3b). The vibrational band pattern of the carbonyl groups in $[\mathbf{3}]^-$ shows a close resemblance to that of $[\mathbf{1}]^{\bullet-}$, and they are similar in energy. Two species are distinct by electron paramagnetic resonance (EPR) and electronic spectra (Figure S5 in the SI). The EPR signals at 77 K are different by 9 G: g = 1.999 for $[\mathbf{1}]^{\bullet-}$ and g = 1.995 for $[\mathbf{3}]^-$.[18] In the visible and near-IR region, two excitations at 931 (sh) and 1033 nm for $[\mathbf{1}]^{\bullet-}$ are observed, which are related to characteristics of $[C_{60}]^{\bullet-}$.[19] They are blue-shifted to 899 (sh) and 996 nm in $[\mathbf{3}]^-$. Two additional bands of $[\mathbf{1}]^{\bullet-}$ at 517 and 781 nm are not observed in $[\mathbf{3}]^-$. Instead, transitions of 611 and 649 nm are the features of $[\mathbf{3}]^-$. The addition of acetic acid to the solution of $[\mathbf{3}]^-$ does not lead to conversion to **1**. Recovery of **1** is completed in the presence of medium acids (Figure S6 in the SI). Successful protonation occurs upon contact with trifluoroacetic acid or hydrochloric acid.

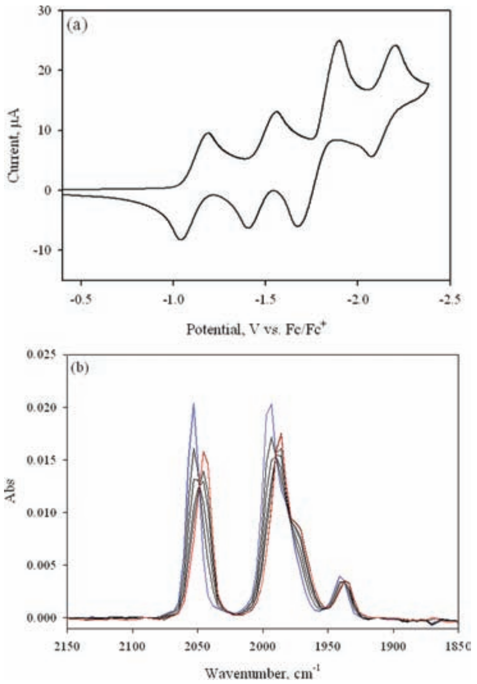

Figure 3. (a) Cyclic voltammogram of **1** (1 mM) in the CH_2Cl_2/*o*-DCB solution (ν = 100 mV/s, 0.1 M *n*-Bu_4NPF_6) at 256 K. (b) Spectral changes from **1** (blue line) to $[\mathbf{3}]^-$ (red line) monitored by in situ IR spectroscopy in tetrahydrofuran at −50 °C.

The geometrical parameters of **1** that were optimized on the B3LYP/6-31G(d) level are in fine agreement with those obtained by X-ray crystallography. The lowest unoccupied molecular orbital of **1** resides predominantly in the fullerene unit, suggesting that the addition of the first electron into **1** is the C_{60}-based event (Figure S7 in the SI). For the singly reduced species, the computed spin density (Figure 4) indicates that the proximal Fe center is partially spin-populated, which is

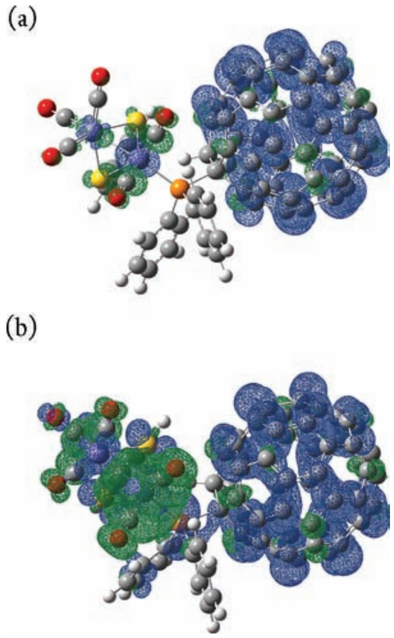

Figure 4. Spin-density plots of (a) $[\mathbf{1}]^{\bullet-}$ and (b) $[\mathbf{1}]^{2-}$.

reflected on the lengthened distance of the Fe−P bond in $[\mathbf{1}]^{\bullet-}$. Compared to the neutral species, the average 11 cm^{-1} shift toward lower energy for the computed ν_{CO} of $[\mathbf{1}]^{\bullet-}$ indicates that the electron density about the Fe center is only perturbed to a small extent and the majority of the spin is localized at the fullerene unit. On the other hand, a bathochromic shift of average 79 cm^{-1} is obtained for the triplet state of the doubly reduced species, $[\mathbf{1}]^{2-}$. Figure 4 displays the spin-density plot of $[\mathbf{1}]^{2-}$ in which the significant extent of spin delocalization onto the Fe center is observed. It is suggested that injection of the electron density from the doubly charged fullerene anion of $[\mathbf{1}]^{2-}$ into the then insulated Fe molecular orbitals occurs. From the results, it is insinuated that electron transfer from the F cluster to the [4Fe4S] unit within the H cluster, followed by electron delocalization into the Fe center, is a key pathway for proton reduction by the catalytic Fe site.

In the present study, it is shown that the redox-active attachment to the Fe_2 core of **1** involves regulation of the electronic structure of the Fe centers, which suggests the essential role of the [4Fe4S] cluster within the H cluster in terms of the electronic factor.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format and additional experimental details and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Holm, R. H.; Kennepohl, P.; Solomon, E. I. *Chem. Rev.* **1996**, *96*, 2239−2314.

(2) Tard, C.; Pickett, C. J. *Chem. Rev.* **2009**, *109*, 2245−2274.

(3) (a) Singleton, M. L.; Bhuvanesh, N.; Reibenspies, J. H.; Darensbourg, M. Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 9492−9495. (b) Ott, S.; Kritikos, M.; Åkermark, B.; Sun, L.; Lomoth, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1006−1009. (c) Olsen, M. T.; Bruschi, M.; De Gioia, L.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **2008**, *130*, 12021−12030. (d) Barton, B. E.; Olsen, M. T.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2008**, *130*, 16834−16835. (e) Liu, Y.-C.; Tu, L.-K.; Yen, T.-H.; Lee, G.-H.; Chiang, M.-H. *Dalton Trans.* **2011**, *40*, 2528−2541. (f) Chiang, M.-H.; Liu, Y.-C.; Yang, S.-T.; Lee, G.-H. *Inorg. Chem.* **2009**, *48*, 7604−7612.

(4) Zampella, G.; Fantucci, P.; De Gioia, L. *J. Am. Chem. Soc.* **2009**, *131*, 10909−10917.

(5) (a) Fontecilla-Camps, J. C.; Volbeda, A.; Cavazza, C.; Nicolet, Y. *Chem. Rev.* **2007**, *107*, 4273−4303. (b) Vincent, K. A.; Parkin, A.; Armstrong, F. A. *Chem. Rev.* **2007**, *107*, 4366−4413.

(6) Tard, C.; Liu, X.; Ibrahim, S. K.; Bruschi, M.; De Gioia, L.; Davies, S. C.; Yang, X.; Wang, L.-S.; Sawers, G.; Pickett, C. J. *Nature* **2005**, *433*, 610−613.

(7) Peters, J. W.; Lanzilotta, W. N.; Lemon, B. J.; Seefeldt, L. C. *Science* **1998**, *282*, 1853−1858.

(8) (a) Liu, Y.-C.; Lee, C.-H.; Lee, G.-H.; Chiang, M.-H. *Eur. J. Inorg. Chem.* **2011**, 1155−1162. (b) Camara, J. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2011**, *133*, 8098−8101. (c) Camara, J. M.; Rauchfuss, T. B. *Nat. Chem.* **2012**, *4*, 26−30.

(9) (a) Xie, Q.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978−3980. (b) Echegoyen, L.; Echegoyen, L. E. *Acc. Chem. Res.* **1998**, *31*, 593−601.

(10) Xie, Q.; Arias, F.; Echegoyen, L. *J. Am. Chem. Soc.* **1993**, *115*, 9818−9819.

(11) Liu, Y.-C.; Tu, L.-K.; Yen, T.-H.; Lee, G.-H.; Yang, S.-T.; Chiang, M.-H. *Inorg. Chem.* **2010**, *49*, 6409−6420.

(12) Cabeza, J. A.; Martinez-Garcia, M. A.; Riera, V.; Ardura, D.; Garcia-Granda, S. *Organometallics* **1998**, *17*, 1471−1477.

(13) Vannucci, A. K.; Wang, S.; Nichol, G. S.; Lichtenberger, D. L.; Evans, D. H.; Glass, R. S. *Dalton Trans.* **2010**, *39*, 3050−3056.

(14) Yamago, S.; Yanagawa, M.; Mukai, H.; Nakamura, E. *Tetrahedron* **1996**, *52*, 5091−5102.

(15) (a) Capon, J.-F.; Gloaguen, F.; Schollhammer, P.; Talarmin, J. *J. Electroanal. Chem.* **2004**, *566*, 241−247. (b) Felton, G. A. N.; Vannucci, A. K.; Chen, J.; Lockett, L. T.; Okumura, N.; Petro, B. J.; Zakai, U. I.; Evans, D. H.; Glass, R. S.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **2007**, *129*, 12521−12530. (c) Felton, G. A. N.; Petro, B. J.; Glass, R. S.; Lichtenberger, D. L.; Evans, D. H. *J. Am. Chem. Soc.* **2009**, *131*, 11290−11291.

(16) Darchen, A.; Mousser, H.; Patin, H. *J. Chem. Soc., Chem. Commun.* **1988**, 968−970.

(17) Dubois, D.; Moninot, G.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Phys. Chem.* **1992**, *96*, 7137−7145.

(18) (a) Boyd, P. D. W.; Bhyrappa, P.; Paul, P.; Stinchcombe, J.; Bolskar, R. D.; Sun, Y. P.; Reed, C. A. *J. Am. Chem. Soc.* **1995**, *117*, 2907−2914. (b) Boulas, P.; D'Souza, F.; Henderson, C. C.; Cahill, P. A.; Jones, M. T.; Kadish, K. M. *J. Phys. Chem.* **1993**, *97*, 13435−13437.

(19) Cliffel, D. E.; Bard, A. J. *J. Phys. Chem.* **1994**, *98*, 8140−8143.